Metal-catalyzed hydrosilylation reaction across C=O bond of aldehydes or ketones is recognized as one of the most practical and environmentally benign protocols in the field of synthetic chemistry because both reduction and protection steps can be realized in a single and an atom-efficient fashion. Therefore, extensive studies on the hydrosilylation reaction have been examined and reported using a transition-metal catalyst, e.g. Rh, Pd, and Pt, in the literature. Although, in the economical aspect, it is highly desirable that the development of the hydrosilylation using inexpensive metal catalyst like Fe or Co, little attention have been paid to the inexpensive transition metal-catalyzed hydrosilylation thus far. In addition, to the best of our knowledge, there are quite limited examples on the hydrosilylation of fluorinated ketones in the presence of a Fe or Co catalyst.

Very recently, our group have focused on the development of effective synthetic methods for organofluorine compounds using such inexpensive cobalt catalyst and we succeeded in Co(CO)$_3$-catalyzed hydrosilylation reaction of fluorine-containing $\alpha$, $\beta$-unsaturated ketones$^1$. During the cobalt-catalyzed hydrosilylation reaction, we observed a drastic difference of the reaction rate between fluorinated and non-fluorinated ketones as the substrate (Scheme 1). In this study, we aimed to figure out distinction of the reaction rate from theoretical calculation.

In Scheme 1 is also shown the possible reaction mechanism for the cobalt-catalyzed hydrosilylation reaction. To gain reasonable explanation for the drastic difference of the reaction rate, we carried out density functional theory (DFT) calculation using Gaussian 09W program. Resulting from the DFT calculation at B3LYP/6-31+G(d,p) levels of theory, the presence of fluorine in the substrate destabilized the initial intermediate (Int-1), rather than the corresponding non-fluorinated one: the Int-1 for fluorinated substrate was found to be ca. 4.5 kcal/mol higher in energy than that for the non-fluorinated one. As a result, the activation energy to cross the transition state (TS-1) in the case of fluorinated one became much smaller value than that in non-fluorinated one ($E^\ddagger_{\text{Fluorinated}}$ = 13.38 kcal/mol and $E^\ddagger_{\text{non-fluorinated}}$ = 21.90 kcal/mol). Judging from the large difference of activation energies, $E^\ddagger_{\text{Fluorinated}}$ vs $E^\ddagger_{\text{non-fluorinated}}$, the cobalt-catalyzed hydrosilylation using fluorinated substrate can proceed extremely faster in comparison with the reaction for non-fluorinated one. In this presentation, we would disclose the results on the cobalt-catalyzed hydrosilylation reactions as well as the mechanistic insight in detail.

**Reference**